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(72) Inventors MALCOLM VICTOR BRANT and
EDWARD FREDERICK EMLEY

(19) THE PATENT OFFICE LONDON

(54) REMOVAL OF NON-METALLIC CONSTITUENTS FROM LIQUID METAL

(71) We, THE BRITISH ALUMINIUM COMPANY LIMITED, a Company registered under the laws of Great Britain, of Norfolk House, St. James's Square, London, S.W.1, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in the removal of non-metallic constituents from liquid metal, particularly but not exclusively liquid aluminium, and especially liquid aluminium intended for the production of ingots for plastic working.

It is well known that liquid aluminium contains varying amounts of non-metallic constituents, i.e. gas and other non-metallic inclusions, and that their presence may give rise to defects in finished products. Many procedures have been proposed for the removal of the gas and inclusions. Thus the gas content may be reduced to an acceptable level by bubbling chlorine, nitrogen or argon through the melt or by treatment of the metal with hexachlorethane. The use of chlorine and hexachlorethane give rise to a fume disposal problem necessitating expensive equipment, whereas with nitrogen the metal may become contaminated through formation of non-metallic inclusions. For removal of inclusions various filtration procedures have been suggested, for example those of British Patent Specifications Nos. 701,273 and 831,637 in which the metal is caused to flow from one chamber to another through a bed of refractory granules of 3—14 ASTM mesh size (0.056—0.250 in aperture), the two chambers being separated by means of a baffle wall below which they are in intercommunication. Such fine filter beds are not well suited to the treatment of metal at the high flow rates required in modern casting practice and moreover they are liable to block up unless the metal to be treated has been first given a chlorine fluxing treatment.

It was proposed in British Patent Specification No. 435,104 to degas a discrete body of liquid aluminium contained in a crucible by agitating the metal in a hydrogen-free (moisture-free) atmosphere particularly by passing dry nitrogen over the metal surface. It was also proposed to use a flux capable of dissolving any aluminium oxide present or formed during the process, the preferred flux containing sodium fluoride. This process has found limited application in the aluminium castings industry, where the metal can be treated in a small crucible, but it has not proved suitable for treatment of metal in the large reverbatory furnaces normally used in the casting of ingots for plastic working where the surface area of liquid metal is large and the metal depth small.

Attempts to degas and clean liquid aluminium in a continuous manner and without generation of objectionable fumes have led to the proposal of British Patent Specification No. 935,191 which describes a flux-washing process in which a liquid metal stream is caused to break up into a plurality of streams by means of a spreader plate located within a layer of liquid salt flux. This process achieves some degree of degassing which is acceptable for the production of aluminium components for certain purposes but we have found that the degassing and cleaning are not sufficiently effective for use in the production of wrought metal for the more critical kinds of application. Moreover the process suffers from the drawback that some of the flux tends to become dispersed in the metal and may pass over into the cast product.

In our British Patent Application No. 45163/69 (Serial No. 1316578) there is described and claimed a process for removing non-metallic constituents from liquid aluminium and its alloys in a continuous manner which comprises flowing such liquid metal through a containing vessel, passing a substantially inert gas into the metal in the vessel while maintaining a liquid flux layer on the metal in the containing vessel, and flowing the metal through a flux trap to remove any

[*Price 25p*]

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flux carried over with the metal. In said process preferably the containing vessel is of such capacity in relation to the metal flow rate that the residence time of the metal in the containing vessel is at least 1½ minutes and preferably at least 3 minutes. Such a process has been shown to be capable of cleaning and degassing any kind of raw untreated aluminium and, at least with the preferred residence time, of producing metal suitable for critical applications.

In operating the above process we have however found that the life of the equipment is largely dependent on that of the porous diffuser tubes used to introduce the purging gas. We have therefore tried introducing nitrogen by means of narrow graphite tubes with a view to causing a high degree of turbulence and by use of a sufficient number of such jets we have operated the process in a very satisfactory manner without the need to use costly and fragile diffuser tubes. With the use of the jets however we found it necessary in order to obtain best results to increase the minimum residence time of the metal in the degassing chamber which, with a given sized unit meant restricting the flow rate of the metal.

JNV

According to the present invention there is provided a process for removing non-metallic constituents from liquid metal in a continuous manner which comprises causing a stream of metal to flow through a containing vessel of such capacity in relation to the metal flow that the residence time of the metal in the containing vessel is at least 0.5 minutes, mechanically agitating the metal therein, and maintaining on the surface of the metal moving through the containing vessel a liquid salt flux in an amount at least equal to 1 lb. per 100 sq. ins. of surface area. The metal may thereafter be passed through a means for stripping entrained flux preferably a bed of refractory granules of such size as to be retained on a ⅜″ aperture screen. Preferably the residence time is in the range 0.5 to 3 minutes. The invention also extends to metal so treated.

The flux preferably consists essentially of ingredients selected from the group consisting of the chlorides and fluorides of the alkali and alkaline earth metals including magnesium, and is thinly fluid at the melting point of the metal. The flux preferably contains not more than 5% alkali fluoride and particularly where sodium is undesirable in the degassed metal it not only contains no NaF but includes magnesium chloride to remove any sodium present.

The required agitation may be effected by means of a stirring device inserted below the surface of the metal in the container and designed to cause the metal to circulate in a plane inclined to the horizontal whereby metal is continually being brought up to the surface from below so that it is brought into contact with the liquid flux. In addition due to the large degree of vertical circulation in the body of the metal the walls of the vessel are rapidly and continuously washed with liquid flux.

The process is preferably carried out in a vessel divided by a baffle wall into ingoing and outgoing chambers which are in intercommunication beneath the baffle wall, with the ingoing chamber forming the containing vessel in which the non-metallic constituents are removed.

The refractory granules may be disposed in the base of the container to a depth sufficient to cover the base of the baffle wall. The outgoing chamber may be filled nearly to the top with the granules; in the ingoing chamber the granules may usefully extend to a height of two to four inches above the base of the baffle.

The granules may consist of materials such as tabular alumina, kyanite, chromite, forsterite, magnesia spinel, magnesium fluoride, periclase, zircon, porous or non-porous graphite, plumbago, or silicon carbide bonded with carbon, silicon nitride or alumina. The granules may be in the form of balls or irregular lumps. They may be moulded into special shapes, e.g. of the kinds used in the chemical industry to pack scrubber towers.

A suitable agitating device is provided by a moulded refractory stirrer which may consist of a long stem bearing one or more blades attached to its lower end and disposed in a plane parallel to the axis of the stem, the stirrer being caused to rotate at a speed of 25—150 rpm and placed in the metal with its axis of rotation inclined to the vertical. Speeds of 50—75 rpm are in general preferred.

Suitable flux compositions for use in accordance with the process of the present invention are as follows, the compositions being expressed in percentage by weight.

	KCl	NaCl	NaF	$MgCl_2$	CaF_2	MgF_2
Flux A	45—65	35—55	—	—	0—10	—
B	35—55	25—45	5—25	—	0—15	—
C	30—55	20—45	—	5—30	0—10	—
D	30—60	—	—	30—50	—	10—20
E	15—35	10—30	—	30—50	0—10	—

Mixtures of KCl and NaCl with small additions of CaF_2 are normally preferred (Flux A). A few per cent of either NaF or $MgCl_2$ may however also be incorporated with a view to lowering slightly the melting point of the metal. Larger additions of NaF further lower

the melting point (Flux B), but a small amount of sodium will then be introduced into the metal. If desired the NaF may be replaced wholly or in part by cryolite but the cryolite content of the flux is preferably kept below 10%. For alloys with high magnesium content it is preferable to use a flux capable of taking sodium from the metal. Suitable fluxes contain $MgCl_2$ (Fluxes C, D and E).

The process thus provides a simple and convenient way of removing sodium and other electropositive metals from aluminium in a continuous manner.

In order that the density of the liquid flux shall remain low in comparison with that of the metal, it is undesirable for substantial amounts of $BaCl_2$ to be incorporated in the flux. It is permissible however to incorporate KF or potassium cryolite into the flux in place of NaF or cryolite. When $MgCl_2$ is also present, the KF will be converted to KCl and the $MgCl_2$ to MgF_2.

In operating the process of the invention we found we were able to effect the same satisfactory cleaning and degassing in much shorter residence times than are required when using the process of British Application No. 45163/69, Serial Number 1316578, even when using nitrogen introduced via porous diffusers. We also found it was unnecessary to control the atmosphere above the flux thus dispensing with the necessity to have a lid over the container or flow hydrogen-free gas above the metal surface. We have thus succeeded not only in eliminating the need for nitrogen and the cost of the diffuser tubes previously used to introduce the gas, but by reducing the residence time required we are able to reduce the size of the equipment needed for a given metal flow rate. We have also found that the cleaning and degassing produced is far greater than with such a known process as that of British Patent Specification No. 935,191.

The operation of the present invention will be further illustrated by reference to the accompanying diagrammatic drawings and the following example. In the drawings, Figure 1 is a section through a metal treatment vessel and stirrer, and Figure 2 parts *a*, *b* and *c* show respectively a side elevation, an end elevation and a plan view of a stirrer.

Figure 1 illustrates one way of carrying out the invention of the present application. A containing vessel in the form of a shallow crucible or bowl 1 is divided by a baffle 2 into an ingoing chamber A and an outgoing chamber B. An exit launder 3 leads from the outgoing chamber to a casting mould. Metal flows continuously from a furnace tap hole, along a launder 4 and falls into the chamber A. A liquid flux layer 5 is provided on the surface of the metal in chamber A. The metal in chamber A is agitated by means of the spade-shaped stirrer 6 rotatable about its axis which is inclined to the vertical and the horizontal. After treatment in chamber A the metal passes through a bed of coarse refractory lumps 7 which extends under the baffle 2 and occupies most of the chamber B. The stirrer is driven by a compressed air motor 8.

EXAMPLE

A metal charge consisting of 5 tons of scrap aluminium sheet was melted, and without any cleaning or degassing treatment the liquid metal produced was caused to flow continuously through the equipment shown in Figure 1. The metal flow rate was 275 lb/min. and the capacity of the degassing chamber A was 150 lb., giving a residence time of metal in this chamber of 0.55 minutes. The surface area of the metal in chamber A was approximately 2.2 sq. ft. 5 lb. of a flux consisting of 52% KCl, 43% NaCl and 5% CaF_2 by weight were applied to the metal surface at the commencement of the cast.

A spade-shaped stirrer with a blade approximately 6 in.×4 in. was used, the blade rotating at a speed of 70 rpm. The refractory granules used were balls of tabular alumina of approximately ¾ in. diameter. Straube-Pfeiffer vacuum gas test samples were taken from metal entering and leaving the equipment. The average number of bubbles obtained in tests on metal entering the equipment was 60 whereas no bubble was obtained in any of the tests made on the treated metal leaving the equipment. The treated metal was found to be very satisfactory as regards inclusion content and gas content, and to be suitable for the production of semi-fabricated products intended for critical applications. No dispersion or carry over of the flux in the metal was observed in any of separate tests carried out with Fluxes A, B and D.

By way of comparison we have treated similar metal charges at flow rates up to 260 lb/min by the process disclosed in British Patents Nos. 1266500 and 1316578 using the equipment shown in Figure 2 of the former specification and have obtained equally satisfactory oxide and gas contents in the treated metal, but the ingoing chamber needed had a capacity of 1,100 lb. of aluminium. Consequently the size of the equipment and therefore the capital costs of operating the process of the present invention are considerably less than for that of the above mentioned process, whilst the operating costs associated with the present invention are much reduced because of the ability to eliminate both the inert gas and the means of introducing it.

If desired the coarse refractory granules may be disposed in a separate vessel, for example a crucible divided into two intercommunicating chambers by means of a baffle wall. Thus the metal may be agitated under the liquid salt flux in one such divided crucible after which it is caused to flow through another

such divided crucible packed with the refractory granules.

The step of agitating the metal under a liquid salt flux may also be carried out in part of a reverberatory furnace or in a forewell thereto, the products of gaseous combustion being preferably shielded from direct contact with the metal under treatment.

The process of the present invention is not limited to the treatment of aluminium. It may be applied for example to magnesium. In this case the equipment used may be made of mild steel, or of heat-resisting steels with high chromium or chromium and manganese content with a view to minimising iron pick-up by the magnesium. The coarse granules will then consist preferably of tabular alumina, graphite or silicon carbide, the latter being preferably avoided where alloys containing zirconium are being processed.

WHAT WE CLAIM IS:—

1. A process for removing non-metallic constituents from liquid metal in a continuous manner which comprises causing a stream of metal to flow through a containing vessel of such capacity in relation to the metal flow that the residence time of the metal in the containing vessel is at least 0.5 minutes, mechanically agitating the metal in the vessel and maintaining on the surface of the metal moving through the vessel a liquid salt flux in an amount at least equal to 1 lb. per 100 sq. inches of surface area.

2. A process according to Claim 1 in which the residence time of the metal in the containing vessel is in the range 0.5 to 3 minutes.

3. A process according to Claim 1 or Claim 2 in which the metal is agitated by a stirring device so as to cause the metal to circulate within the vessel at an angle both to the horizontal and the vertical.

4. A process according to Claim 3 in which the metal is agitated by a stirring device rotating about its axis, which axis is inclined both to the horizontal and the vertical.

5. A process according to Claim 3 or Claim 4 in which the stirring device has a stem and at least one blade adjacent the lower end thereof.

6. A process according to any one of Claims 1—5 in which the stirring device for causing the mechanical agitation is rotated at a speed in the range 25—150 rpm.

7. A process according to Claim 6 in which the stirring device is rotated at a speed in the range 50—75 rpm.

8. A process according to any one of Claims 1—7 in which the flux consists essentially of ingredients selected from the group consisting of the chlorides and fluorides of the alkali and alkaline earth metals including magnesium and is thinly fluid at the melting point of the metal.

9. A process according to any one of Claims 1—8 in which the metal from which non-metallic constituents have been removed is passed through a means for stripping entrained flux therefrom.

10. A process according to Claim 9 in which the means for stripping entrained flux comprises a bed of refractory granules of such a size as to be retained on a $\frac{3}{8}''$ aperture screen.

11. A process according to any one of Claims 1—10 in which the containing vessel in which the non-metallic constituents are removed is formed by an ingoing chamber of a vessel having ingoing and outgoing chambers divided by a baffle wall, the metal in the ingoing chamber being covered with the flux layer and the chamber being in intercommunication beneath the baffle wall.

12. A process according to Claim 11 together with Claim 10 in which the granules are located in the outgoing chamber and at least to the level of the lower edge of the baffle wall in the ingoing chamber.

13. A process according to any one of Claims 1—12 in which the metal is aluminium.

14. A process for removing non-metallic constituents from liquid metal in a continuous manner according to Claim 1 and substantially as described herein.

15. Metal processed by the process of any one of Claims 1—14.

For the Applicants:—
RAWORTH, MOSS & COOK,
Chartered Patent Agents,
36, Sydenham Road,
Croydon, Surrey.
and
75 Victoria Street,
Westminster,
London, S.W.1.

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FIG. 1

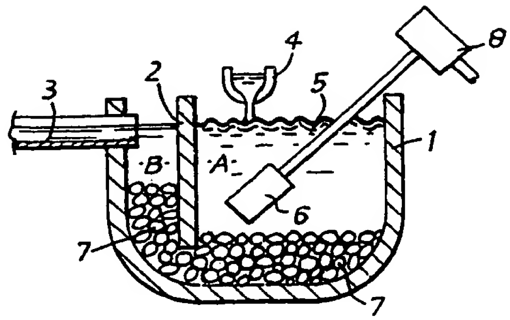
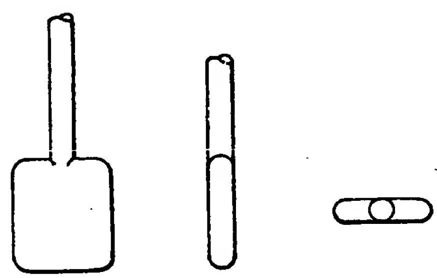


FIG. 2



(a) (b) (c)